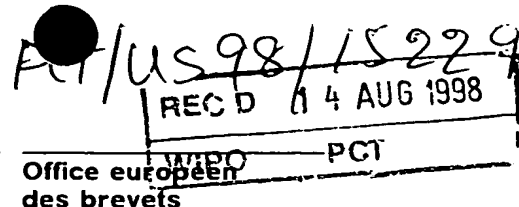




Eur päisches  
Patentamt

European  
Patent Office

Office européen  
des brevets



Bescheinigung

Certificate

Attestation

09/462971

Die angehefteten Unterla-  
gen stimmen mit der  
ursprünglich eingereichten  
Fassung der auf dem näch-  
sten Blatt bezeichneten  
europäischen Patentanmel-  
dung überein.

The attached documents  
are exact copies of the  
European patent application  
described on the following  
page, as originally filed.

Les documents fixés à  
cette attestation sont  
conformes à la version  
initialement déposée de  
la demande de brevet  
européen spécifiée à la  
page suivante.

Patentanmeldung Nr. Patent application No. Demande de brevet n°

97202335.2

## PRIORITY DOCUMENT

SUBMITTED OR TRANSMITTED  
BUT NOT IN COMPLIANCE  
WITH RULE 17.1(a) OR (b)

Der Präsident des Europäischen Patentamts:  
Im Auftrag

For the President of the European Patent Office

Le Président de l'Office européen des brevets  
p.o.

W.G.F. VAN ROOSMALEN

DEN HAAG, DEN  
THE HAGUE, 24/11/97  
LA HAYE, LE



**Eur päisches  
Patentamt**

**European  
Patent Office**

**Office européen  
des brevets**

**Blatt 2 der Bescheinigung  
Sheet 2 of the certificate  
Page 2 de l'attestation**

Anmeldung Nr.  
Application no  
Demande n° 97202335.2

Anmeldetag:  
Date of filing: 25/07/97  
Date de dépôt:

Anmelder:  
Applicant(s)  
Demandeur(s)  
DU PONT DE NEMOURS INTERNATIONAL S.A.  
1218 Le Grand-Saconnex (Genève)  
SWITZERLAND

Bezeichnung der Erfindung  
Title of the invention  
Titre de l'invention  
Polyolefin compositions

In Anspruch genommene Prioritäten: / Priorities claimed / Priorité(s) revendiquée(s)

Staat  
State  
Pays

Tag  
Date  
Date

Aktenzeichen  
File no  
Numéro de dépôt

Internationale Patentklassifikation  
International Patent classification  
Classification internationale des brevets  
C08L23/00

Am Anmeldetag benannte Vertragsstaaten  
Contracting states designated at date of filing AT/BE/CH/DE/DK/ES/FI/FR/GB/GR/IE/IT/LI/LU/MC/NL/PT/SE  
Etats contractants désignés lors du dépôt

Bemerkungen  
Remarks  
Remarques

TitleFlame retardant Polyolefin Compositions

5

Background of the InventionField of Invention:

10

This invention relates to polyolefin compositions and more particularly to such compositions which are halogen-free and flame retardant, and to shaped articles made from them.

15

Background Discussion:

Polyvinyl chloride (PVC) products have been on the market for many years and are commonly used in a large variety of applications. With the trend toward a chlorine-free environment, certain market segments such as the construction and wires and cables industries are in need of an alternative to PVC. Several halogen-free flame-retardant compounds are already available on the market but require difficult mixing processes. These compounds often need to be produced by specialized compounders, as the wire and cable and floor tile producers, themselves, often do not have the expertise.

25

For wire and cable applications, halogen-free flame-retardant materials are desirable to provide both insulation and jacketing in low-voltage cables in areas where it is necessary to avoid the generation of hazardous gases in the event of fire. Such areas where halogen-free low-voltage cables are useful include hotels, hospitals, schools, theaters and other such public spaces.

30

Important characteristics for jacketing materials is that they are highly flame retardant, good heat performance and good physical properties.

35

U.S. Patent Nos. 4,948,669, 4,430,468, 4,434,258, 4,673,620, 4,701,359 disclose PVC-free compositions that are suitable for use as coatings for electrical cables. These compositions contain several components that are similar to those described herein, but lack, i.e., the terpolymer described herein.

### Summary of the Invention

According to the present invention there is provided a flame retardant, halogen-free polymer composition comprising a blend of

- 5
- (1) ethylene vinyl acetate carbon monoxide terpolymer containing 30-90% by weight ethylene, 10-70% by weight vinyl acetate and 1-40% by weight carbon monoxide;
- 10
- (2) an ethylene vinyl acetate or polyolefin selected from the group consisting of (a) ethylene vinyl acetate containing 25-90% by weight ethylene and 10-75% by weight vinyl acetate, (b) a linear low density polyethylene, (c) a low density polyethylene, (d) a very low density polyethylene and (d) a high density polyethylene; and mixtures thereof;
- 15
- (3) an ethylene vinyl acetate or polyolefin selected from the group consisting of (a) ethylene vinyl acetate containing 25-90% by weight ethylene and 10-75% by weight vinyl acetate, (b) a linear low density polyethylene, (c) a low density polyethylene, (d) a very low density polyethylene and (d) a high density polyethylene; and mixtures thereof; each of which is grafted with 0.05-3 % by weight of a carboxylic acid or an anhydride thereof; and
- 20
- (4) an inorganic filler.
- 25
- Common additives which may be included in the composition of the present invention include antioxidants, titanium dioxide (for UV resistance and to give a white color to the product), processing aids like zinc stearate and UV stabilizers.

### Detailed Description of the Invention

- 30
- The present invention relates to flame retardant, halogen-free thermoplastic polymer blends which are useful in wire and cable coatings or in sheet form such as for use in floor tiles. These blends generally are formed by combining an ethylene vinyl acetate carbon monoxide (EVACO) terpolymer, an ethylene vinyl acetate (EVA) copolymer
- 35
- or polyolefin selected from EVA copolymer, a linear low density polyethylene, a low density polyethylene, a very low density polyethylene, a high density polyethylene and mixtures thereof, an ethylene vinyl acetate (EVA) copolymer or polyolefin selected from EVA copolymer, a linear low density polyethylene, a low density polyethylene, a very low density polyethylene, a high density polyethylene and

mixtures thereof, each of which is grafted with a carboxylic acid or anhydride thereof, and an inorganic filler.

5 Polymer blends according to the present invention can be formed into wire and cable coatings or sheet form for uses such as for floor tiles, and have many properties comparable to polyvinyl chloride (PVC) containing blends, but are free from halogen.

10 Unless otherwise stated, percentage weight ranges for each of the components in the composition of the present invention are calculated exclusive of any additives which may be present.

The EVACO terpolymer (component (1)) useful in this invention preferably contains 30-90% by weight of ethylene, 10-70% by weight of vinyl acetate and 1-20% by weight of carbon monoxide, more preferably 55-65% by weight of ethylene and 20-15 30% by weight of vinyl acetate and 5-15% by weight carbon monoxide. In general, these EVACO's have a melt flow index (MFI) in the range of 1-50 g/10 min., preferably in the range of 10-40 g/10min. as determined by ASTM D-1238 (measured at 2,16 kg and 190 °C) and are well-known in the art.

20 Component (1) preferably comprises 1-60% by weight of the composition of the present invention, more preferably 5-25% by weight, still more preferably 5-15% by weight.

25 The EVA copolymer when used as component (2) in this invention preferably contains 25-90% by weight of ethylene and 10-75% by weight of vinyl acetate, more preferably 55-75 % by weight of ethylene and 15-30 % by weight of vinyl acetate. In general, these EVA's have a melt flow index (MFI) in the range of 0.05-100 g/10 min., preferably less than 50 g/10min. as determined by ASTM D-1238 (measured at 2,16 kg and 190 °C) and are well-known in the art.

30 The polyolefins when used as component (2) in general will have a melt flow index (MFI) in the range of 0.05-100 g/10 min., preferably less than 50 g/10min. as determined by ASTM D-1238 (measured at 2,16 kg and 190 °C) and are well-known in the art.

35 Component (2) preferably comprises 1-50% by weight of the composition of the present invention, more preferably 5-25% by weight, still more preferably 10-20% by weight.

Component (3) is as defined as for component (2), but is further grafted with 0.05-3 % by weight of a carboxylic acid or anhydride thereof, preferably maleic anhydride. In general, component (3) will have a melt flow index (MFI) in the range of 0.05-100 g/10 min., preferably less than 20 g/10min. as determined by ASTM D-1238  
5 (measured at 2,16 kg and 190 °C).

Component (3) preferably comprises 1-40% by weight of the composition of the present invention, more preferably 1-15% by weight, still more preferably 3-10% by weight.  
10

Component (4) is an inorganic filler. Suitable inorganic fillers are known in the art; preferred ones will also possess flame retardant characteristics. Specific, preferred inorganic fillers include aluminum trihydrate, magnesium hydroxide, calcium carbonate, calcinated clay, talcum, ammonium polyphosphate and mixtures thereof.  
15

Component (4) preferably comprises 20-85% by weight of the composition of the present invention, more preferably 50-75% by weight, still more preferably 60-70% by weight.  
20

In addition to its polymer and flame retardant filler components, the composition of the present invention can be blended with common additives such as antioxidants, UV stabilizers, lubricants (e.g., oleamide), antiblocking agents, antistatic agents, waxes, pigments, titanium dioxide, talc and other processing aids (e.g., zinc stearate ) known  
25 in the polymer compounding art. The additives may comprise up to about 10 weight percent of the total composition based on polymer components, flame retardant fillers plus additives.

The blends of the invention can be prepared by mixing the polymeric ingredients flame retardant fillers and optional additives by use of conventional masticating equipment, for example, a rubber mill, Brabender Mixer, Banbury Mixer, Buss-ko kneader, Farrel continuous mixer or twin screw continuous mixer. Mixing times  
30 should be sufficient to obtain homogeneous blends and a proper reaction between maleic anhydride groups and the flame retardant fillers (component (4)). Typically, mixing times of about 5 minutes and mixing temperatures of 160 °C are satisfactory.  
35 If the polymer blend is non-homogeneous, additional mixing is required.

The invention can be further understood by the following examples in which parts and percentages are by weight or in parts per hundred rubber (phr) and temperatures are in degrees Celsius.

5

### Examples 1-4

#### Legend

- MFI = melt flow index
- 10 EVACO = ethylene-vinyl acetate carbon-monoxide
- EVA = ethylene vinyl acetate
- EVA+MAH = ethylene vinyl acetate grafted with maleic anhydride
- HDPE+MAH = high density polyethylene grafted with maleic anhydride
- ATH = aluminum trihydrate
- 15 MAH = maleic anhydride

#### Procedure

20 A blend is prepared by melt-compounding the following components in the proportions set forth in Table 1 below.

- EVACO (71.5% ethylene, 20.5% vinyl acetate and 8% carbon monoxide) having a MFI (190°/2.16 kg) of 15
- EVA (72% ethylene and 28% vinyl acetate) having a MFI (190°/2.16 kg) of 3.0
- 25 • EVA+MAH (72% ethylene and 28% vinyl acetate grafted with 1.5 % MAH) having a MFI (190°/2.16 kg) of 1.4
- HDPE+MAH (grafted with 0.9 % MAH) having a density of 0.955 g/cc and a MFI (190°/2.16 kg) of 2.0
- VLDPE having a density of 0.902 g/cc and a MFI (190°/2.16 kg) of 1.0
- 30 • antioxidant - phenolic type available under the name IRGANOX 1010 from Ciba Specialty Chemicals

Melt compounding is carried out on a two roll mill with batches from 100 grams at 150-170 °C for ca. 5 minutes. The milled product is formed into a testing plaque in a 35 hydraulic press at 150-170 °C for 5 minutes. Afterwards stress-strain testing (ASTM D-412), Limited Oxygen Index i.e. LOI (ASTM D 2863) and Knife Penetration at 80 and 90 °C (IEC 540 Item 10.1) are carried out. Results are shown in Table 1.

Table 1

<u>Example numbers</u>		<u>1</u>	<u>2</u>
5	EVACO	10	10
	EVA	16	13
	EVA+MAH	9	4
	HDPE+MAH	-	4
	VLDPE	-	4
10	ATH	64.7	64.7
	Antioxidant	0.3	0.3
	Tensile strength (MPa)	14.6	15.7
	Tensile elongation (%)	150	140
	Knife Penetr. at 80 °C (%)	80	0
15	Knife Penetr. at 90 °C (%)	100	0
	LOI (%)	38	35

One can see that the formulation containing HDPE+MAH and VLDPE show particularly lower knife penetration values (better heat performance) but lower flame retardancy than the formulation without. For some wire and cable applications, heat performance can be of major importance while in others flame retardancy is the most important criteria .



Claims

1. A flame retardant, halogen-free polymer composition comprising a blend of
  - (1) ethylene vinyl acetate carbon monoxide terpolymer containing 30-90% by weight ethylene, 10-70% by weight vinyl acetate and 1-40% by weight carbon monoxide;
  - (2) an ethylene vinyl acetate or polyolefin selected from the group consisting of (a) ethylene vinyl acetate containing 25-90% by weight ethylene and 10-75% by weight vinyl acetate, (b) a linear low density polyethylene, (c) a low density polyethylene, (d) a very low density polyethylene and (d) a high density polyethylene; and mixtures thereof;
  - (3) an ethylene vinyl acetate or polyolefin selected from the group consisting of (a) ethylene vinyl acetate containing 25-90% by weight ethylene and 10-75% by weight vinyl acetate, (b) a linear low density polyethylene, (c) a low density polyethylene, (d) a very low density polyethylene and (d) a high density polyethylene; and mixtures thereof; each of which is grafted with 0.05-3 % by weight of a carboxylic acid or an anhydride thereof; and
  - (4) an inorganic filler.
2. A blend according to claim 1 wherein component (1) comprises 1-60 % by weight of the blend, component (2) comprises 1-50 % by weight of the blend, component (3) comprises 1-40 % by weight of the blend, and component (4) comprises 20-85% by weight of the blend.
3. A blend according to claim 1 wherein component (1) comprises 5-25% by weight of the blend, component (2) comprises 5-25% by weight of the blend component (3) comprises 1-15% by weight of the blend, and component (4) comprises 50-75% by weight of the blend.
4. A blend according to claim 1 wherein component (1) comprises 5-15% by weight of the blend, component (2) comprises 10-20% by weight of the blend component (3) comprises 3-10% by weight of the blend, and component (4) comprises 60-70% by weight of the blend.

5. A blend according to claim 1 wherein component (4) is aluminum trihydrate, magnesium hydroxide, calcium carbonate, calcinated clay, talcum, ammonium polyphosphate or a mixture thereof
- 5 6. A shaped article formed from a blend according to claim 1.

Title

5

Flame retardant Polyolefin Compositions

Abstract of the Disclosure

10

Halogen-free polyolefin blends are provided which are flame retardant and are particularly useful in replacing polyvinyl chloride for production of different products such as coatings for wire and cable and sheets for floor tiles. The blends comprise (1) ethylene vinyl acetate carbon monoxide terpolymer, (2) an ethylene vinyl acetate or polyolefin; (3) an ethylene vinyl acetate or polyolefin grafted with a carboxylic acid or an anhydride thereof; and (4) an inorganic filler.

